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Semi-Annual Status Report ~~for Period~~
March 1, 1964 - July 31 (Aug. 31), 1964

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During the report period the chief activities have fallen into the following two general categories:

A. Paramagnetic Resonance of Rare Earths. Further perfection and test of the equipment; experiments on Ho^{3+} in $LaCl_3$ and Er^{3+} in CaF_2.

B. Direct determination of relaxation times of excited states of rare earth ions in crystals. Completion of experimental set-up and results.

The two subjects, though related, will be taken up separately, as they involve considerably different experimental techniques.

A. Paramagnetic Resonance Studies

The equipment for the paramagnetic resonance had to be built up from nothing. Previous reports have dealt with the extended delays due to delivery of faulty equipment or late delivery. The equipment is now in good working order. The cryostatic section is in the process of being redesigned in order to make use of the experience obtained with the present system.

The work carried out during the present report period was designed chiefly to test the capabilities of the system by obtaining the regular paramagnetic resonance at liquid helium temperature of Ho^{3+} in $LaCl_3$ and of Er^{3+} in CaF_2. These substances were chosen because there was a great deal of information available on them from other sources, particularly optical experiments. Some details will be presented below. In addition, paramagnetic resonance of optically excited states of Er^{3+} in $LaCl_3$ was tried. This was done with the present cryostat, which is admittedly inadequate. For this reason there were no positive results, but the experience was valuable for the redesign.

(1). Ho^{3+} in $LaCl_3$. Ho^{3+}, with an atomic mass 165 and a nuclear spin $7/2$, has the distinction of being the only rare earth ion which has a resolvable nuclear hyperfine structure in its optical crystal spectrum. A great deal of information obtained from the optical spectrum in our laboratory is available. Hutchison and Wong (J. Chem. Phys. 29, 754 (1958)) have studied the paramagnetic resonance to a limited extent.

UNPUBLISHED PRELIMINARY DATA

The available crystal (0.1% Ho in $LaCl_3$) gave too weak resonance to obtain all the desired results and was studied at a time when the equipment was not yet in the best working order. Nevertheless, significant results were obtained, which show that the set-up is capable of excellent performance.

Fig. 1 shows at the left the eight field free doubly degenerate hyperfine structure components and how they split in a magnetic field up to 800 gauss. The vertical lines give the observed transitions and the magnetic fields at which resonance is observed. The two broken lines are forbidden transitions, for which $\Delta m_I \neq 0$ ($m_I = I_z$). This information, which undoubtedly can be improved upon, makes it possible to obtain not only the previously known electronic splitting factor, s_z, but also the contributions of the nuclear magnetic moment and the electric quadrupole moment to the nuclear hyperfine structure separately. These are the factors A = 0.532 and P = 0.0014 in the spin Hamiltonian. The optical measurements show a pronounced quadratic term, but as they always give the differences between two states, it is important to obtain an independent value for the ground state.

(2). Er^{3+} in CaF_2. This example was chosen because in the past a great deal of work has been done on rare earth ions in the cubic CaF_2 lattice. These have indicated that the rare earth ion can enter at several sites with different symmetry. This has complicated both the paramagnetic resonance and optical spectra and in no case has there been a satisfactory explanation of the observed facts. Fig. 2 shows a summary of the observations. The crystal is rotated in the magnetic field about one of the four-fold axes and the abscissae represent the aximuth. At each orientation all the resonances are observed. These are indicated completely only near 40° and other data near 132°. It is seen that some resonances are isotropic, others show tetragonal symmetry. Points of trigonal symmetry have been observed by others with a different orientation of the crystal. Crystal field calculations have been carried out successfully to account for most of the facts.

These are, however, in contradiction to the explanation of some of the optical transitions, so that this problem requires further study before it is completely understood. Here a combination of paramagnetic resonance and optical absorption and fluorescence methods are essential. We are now in a position to carry out such combined studies. Table I gives a sample of the numerical results that are obtained.

B. Direct Determination of the Relaxation Times of Excited States of Rare Earth Ions.

The principle is as follows:

(a) A crystal containing a particular rare earth ion is illuminated by a controlled light flash of short duration.

(b) After the termination of the flash, the intensity of the fluorescence spectrum is measured as function of the time. The decay is usually exponential and a relaxation time can be determined.

(c) This relaxation time, which is the mean life of the excited state, is usually determined by the interaction of the ion with the crystal lattice and provides important clues for the mechanism of the interaction.

Our laboratory has pioneered about eight years ago (Steinhaus, Hall) in the development of modern methods for such measurements. The methods used at that time fell short in several respects of the requirements of the present problem. These are: excitation by monochromatic flashes of microseconds duration; measurement of the decay time of single lines or narrow groups of lines.

In the older experiments no attempts had been made to provide monochromatic flashes and only the decay of the total light could be measured. The new requirements necessitated a completely different electronic system, as the old one could not take care of the greatly reduced intensity. The new equipment, developed by Mr. G. Barasch for this project, works as follows:

(1) A very bright flash of white light, usually of about 10 microseconds duration, is produced by a capacitor discharge through a xenon-filled flash tube.
(2) The light flash is passed through a very fast (F:1.5) monochromator which isolates a spectral band of about 100A width at the selected absorption band of the crystal.
(3) The monochromatic flash emerging from the monochromator illuminates the crystal, which ordinarily is in a liquid nitrogen or helium cryostat.
(4) The resultant fluorescence is passed through a second monochromator of high resolution to a photomultiplier.
(5) The photomultiplier is activated by a controlled voltage pulse. The recording circuit therefore is active during an interval of about 20 microseconds, the beginning of which can be set to any adjustable time after the end of the exciting light pulse.
(6) The whole process is iterative and the output records the average over successive cycles, thus greatly improving the signal to noise ratio.
(7) In order to compensate for differences in intensity between successive cycles, a second photomultiplier tube monitors the light output from the flash tube and the system records the ratio between the two photomultipliers.

In the design of the equipment there was always the need of a compromise between the signal to noise ratio and the spectral and time resolution desired.

In this report only the essentials of the system are mentioned, and the many details of the design and construction,on the perfection of which the results depend, will be left for a more definitive report at the end of the work.

Fig. 3 shows a schematic diagram of the whole system, Fig. 4 a block diagram of the control system for the flash tube, Fig. 5 the same for the recording circuit.

The following enumeration gives the present procedure for each

measurement.

1. The excitation monochromator is set to the approximate wave length of excitation.

2. The fluorescence is found by using the signal channel, gated early during the afterglow but after the light source is off. The fluorescence monochromator is set to its peak.

3. The excitation monochromator is reset to peak the fluorescence intensity. All wave lengths are recorded.

4. The reference channel is turned on; its sensitivity is set to record the reference light in the upper half of the strip chart.

5. The signal channel is moved in time toward the excitation pulse until the signal is in a definitely nonexponential region. This will be recorded as the first point.

6. Signal channel gate lengths are set according to the estimated lifetime; if there is still measurable fluorescence after a delay of 100 μ sec, a 20 μ sec gate is generally used.

7. Reference channel gate lengths are set to cover the exciting pulse of light. Generally 30 μ sec is adequate.

8. The time constant is set from experience to give noise limited to a few percent of full scale. Both channels are set the same.

9. Sequence unit Section B is allowed to operate the shutter and relays, and the recording of data may be started.

10. The signal channel delay time is set appropriately. The first delay time is chosen as in (5) above. The successive delay lines are chosen to give about a 50% change in the net signal. (This is varied as conditions merit.)

11. There must now be a wait for the various averaging networks to reach equilibrium. This time is taken as three lifetimes (3RC) for each separate network. During this time the recorder chart runs and records the amplifier zeros.

12. After the wait, the recorder records the signals as dictated by the sequence unit. The time of recording is generally 1.5 to 2 times longer than the wait. (Note: Steps (11) and (12) are timed automatically.)

13. For each point, the signal channel gain is set to the maximum possible.

14. Written on the recorder trace for each point are:

(a) The delay time
(b) The signal channel gain
(c) Changes in time constant
(d) Other pertinent data

15. The last point recorded shows a signal channel difference of a few percent of dark current.

The following steps take place later in the reduction of the data:

16. An average recorder reading is obtained for:

(a) Signal channel light-plus-dark
(b) Signal channel dark
(c) Reference channel light
(d) Reference channel zero

17. Differences are taken and converted into current.

18. For each point, $\log_e$ (Signal channel light current/Reference channel light current) is obtained.

19. A plot of this number versus delay time should yield a straight line and several examples are shown in Fig. 6.

20. The slope of this line is the reciprocal lifetime.

Table II gives a sample of results obtained so far. This is entirely preliminary, as the perfecting of the equipment, which was very time-consuming, required most of the time. Earlier results were taken for the detection of possible sources of error rather than to obtain usable results. The description given above shows that the procedure is quite elaborate.

Barring the discovery of unforeseen trouble, the equipment seems to be now in good working order, and Fig. 6 gives a sample of what can be achieved now. The three traces have been taken with the same crystal at the same temperature but with radiation from different excited states with different exciting radiation. The wave length of the exciting radiation and the designation of the band of Ho^{3+} that is excited have been listed in the first line with each curve. The second line gives the fluorescence band and the transition, and the third line the lifetime.

It is quite evident that without the refinements of the present system no significant results could have been obtained, as without the spectral resolution only an indefinite average would have been recorded, without any physical significance.

The results which are to be obtained in this experiment will be useful in several ways. For the paramagnetic resonance of excited states, the main task of Section A, it is very important that the optical pumping will produce a large population of the particular excited state. This can only happen if the relaxation time is not too short. The lifetimes themselves will be important for the elucidation of the various possible electron lattice interaction processes.

This report, which was not due until August 31, has been advanced a month, partly because August is the vacation month for most of the personnel, partly to have an account of the work carried out up to date for presentation with the request for renewal.

Table I

Experimental Results: Er^{3+} in CaF_2

Line	D. P. P. H. resonance (MHz) for calibration	Erbium resonance (MHz)	s in cm^{-1}
Isotropic	13.943	4.1291	6.7656
Isotropic	13.943	4.1086	6.7993
Isotropic	13.936	4.1190	6.7788
	13.936	4.1204	6.7765
Mean Isotropic $s = 6.780 \pm 0.008$			
Tetragonal Lines (Crystal rotated about [011] axis)			
$\perp$ [100] axis	13.936	4.4637	6.2584
(Single line)	13.936	4.4582	6.2630
	13.943	4.4463	6.2594
Mean Tetragonal $s_\perp = 6.258 \pm 0.002$			
$\parallel$ [100] axis	13.943	3.5834	7.7959
(Single line)	13.936	3.5808	7.8016
	13.936	3.5883	7.7852
Mean Tetragonal $s_\parallel = 7.794 \pm 0.006$			
$\perp$ [100] axis	13.943	4.4660	6.2552
(Double line)	13.936	4.4400	6.2880
In (100) plane	13.943	3.9498	7.0727
45° to [010] axis	13.936	3.9287	7.1072
(Double line)			
For the double lines, $s_\parallel$ can be calculated with the formula: $s(45°) = \sqrt{\frac{1}{2}(s_\parallel^2 + s_\perp^2)}$			
$s_\parallel$	13.943	—	7.805
(Double line)	13.936	—	7.841

Table II

Some typical lifetimes (in microseconds)

Ion	Lattice	State	Percent	4°K	77°K	Percent	4°K	77°K	300°K
Pr	$LaCl_3$	$^3P_1$	1	5.2		2	5.2	15	
		$^3P_0$	1	13.7		2	13.5	18	
		$^1D_2$	1	7.7		2	a		
Pr	$LaCl_3$	$^3P_0$	25	12.2		50	10.5		
Pr	$LaCl_3$	$^3P_0$	100	9.5	9				
Nd	$LaCl_3$	G	1	78					
		E	1	55					
		D	1	28					
Eu	$LaCl_3$	$^5D_2$	1		(420)				
		$^5D_1$	1		(530)				
		$^5D_0$	1		(670)				
Tb	$LaCl_3$	$^5D_3$	2		(530)				
		$^5D_4$	2		(1302)				
Ho	$LaCl_3$	M	1	31.3		2	34.3	<10	
		K	1	(35)	(38)	2	(30)	37	
		J	1	c		2	a	36	
		F	1	99	112	2	111	118	
		E	1	271	(330)	2	287	270	
		D	1	215	318	2	205	234	
Er	$LaCl_3$	L	<10		15				
		K	<10		25				
Er	$GdCl_3$	L	2		18.5				
		K	2		117				
		E	2		420				
Er	Y_2O_3	K				1		218	114
		E				1		153	83

(Values between parentheses are less reliable).

a. Fluorescence weak, short lifetime.

Fig. 1

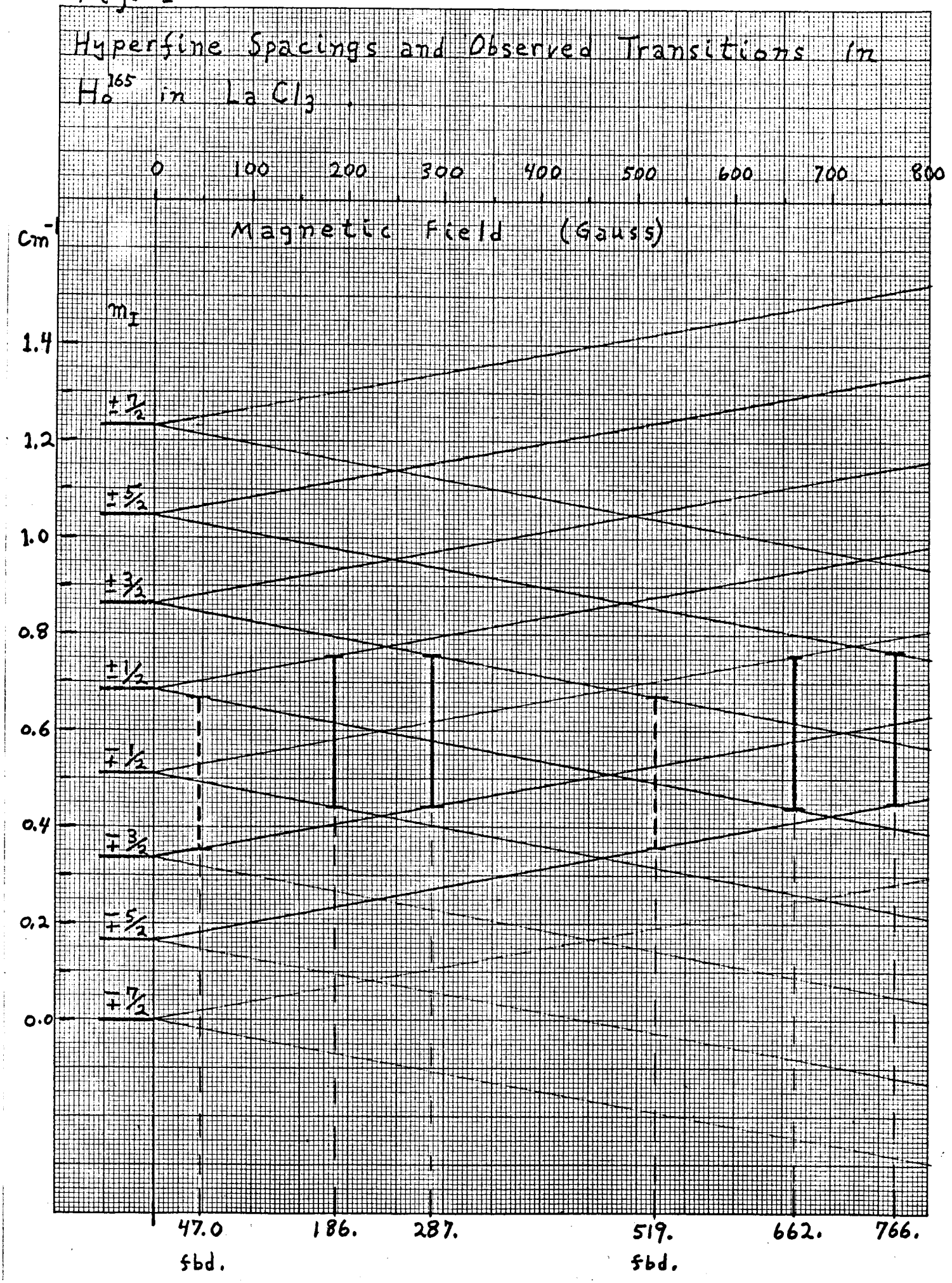
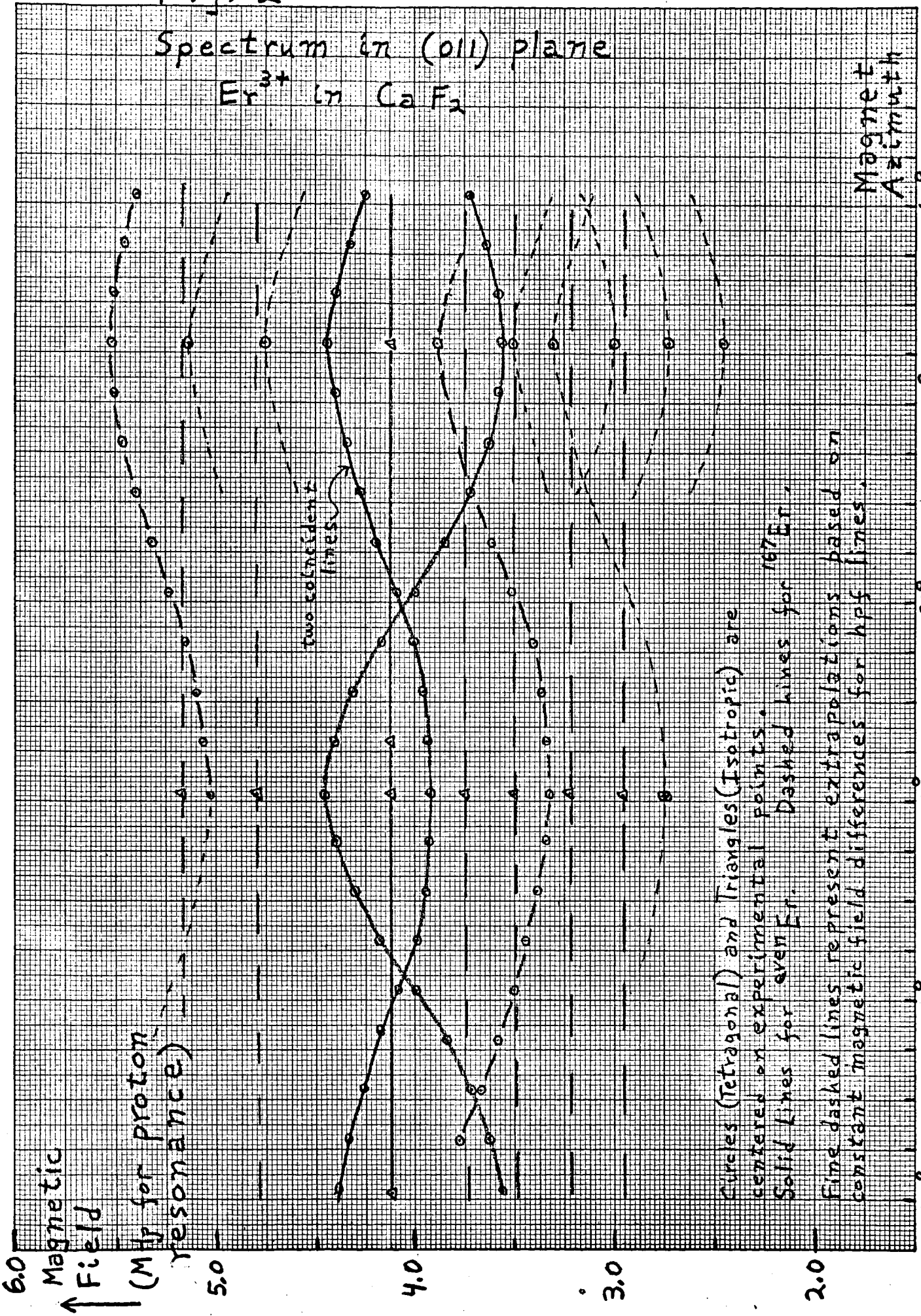

Hyperfine Spacings and Observed Transitions in Ho^{165} in $LaCl_3$.
0
100
200
300
400
500
600
700
800
Magnetic Field (Gauss)
cm^{-1}
m_I
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
$\pm 7/2$
$\pm 5/2$
$\pm 3/2$
$\pm 1/2$
$\mp 1/2$
$\mp 3/2$
$\mp 5/2$
$\mp 7/2$
47.0
fbd.
186.
287.
519.
fbd.
662.
766.

Fig. 2

Spectrum in (011) plane

Er^{3+} in CaF_2



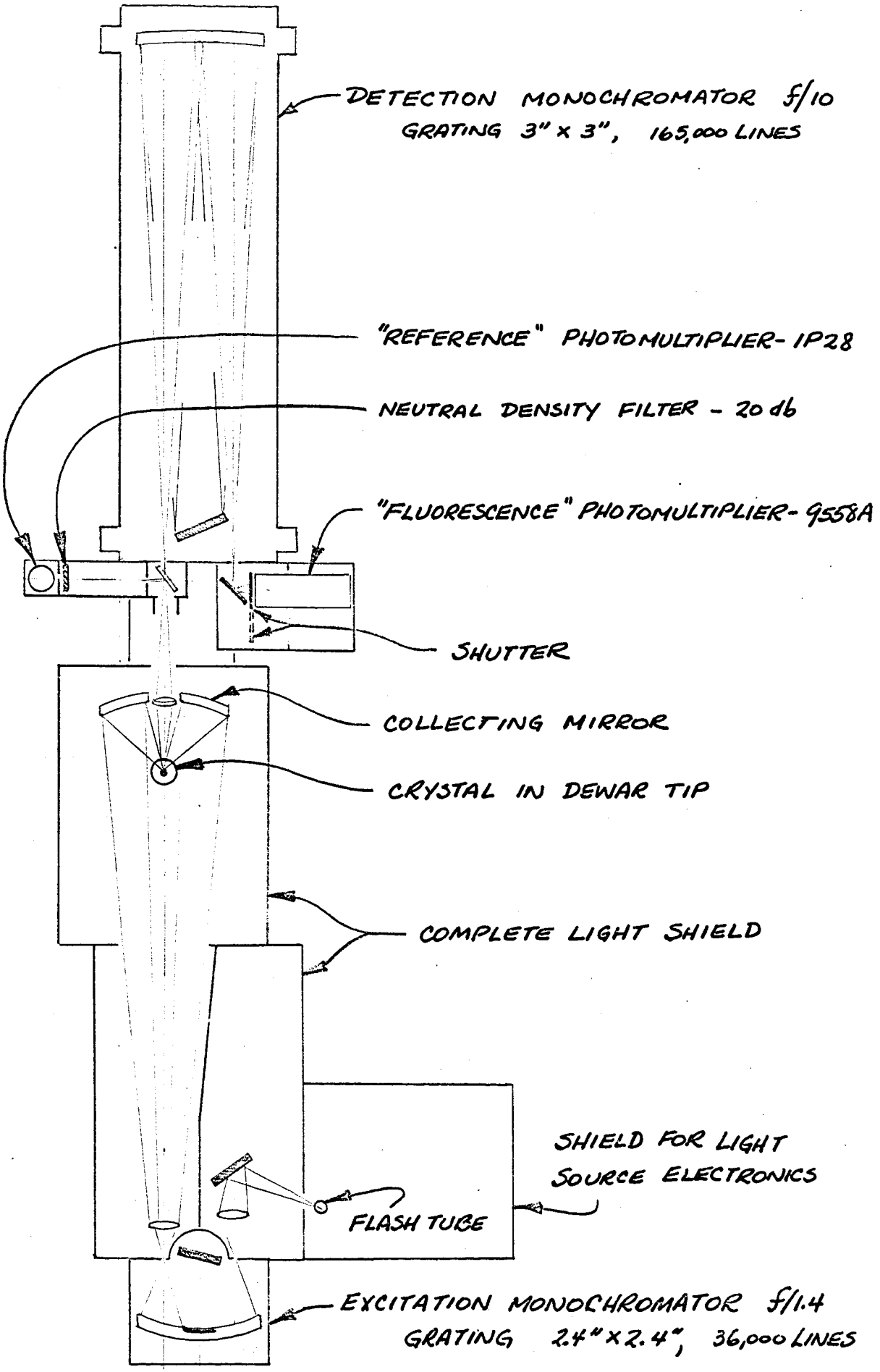

DETECTION MONOCHROMATOR f/10
GRATING 3" x 3", 165,000 LINES
"REFERENCE" PHOTOMULTIPLIER- 1P28
NEUTRAL DENSITY FILTER - 20 db
"FLUORESCENCE" PHOTOMULTIPLIER- 9558A
SHUTTER
COLLECTING MIRROR
CRYSTAL IN DEWAR TIP
COMPLETE LIGHT SHIELD
SHIELD FOR LIGHT SOURCE ELECTRONICS
FLASH TUBE
EXCITATION MONOCHROMATOR f/1.4
GRATING 2.4" X 2.4", 36,000 LINES

FIG. 3

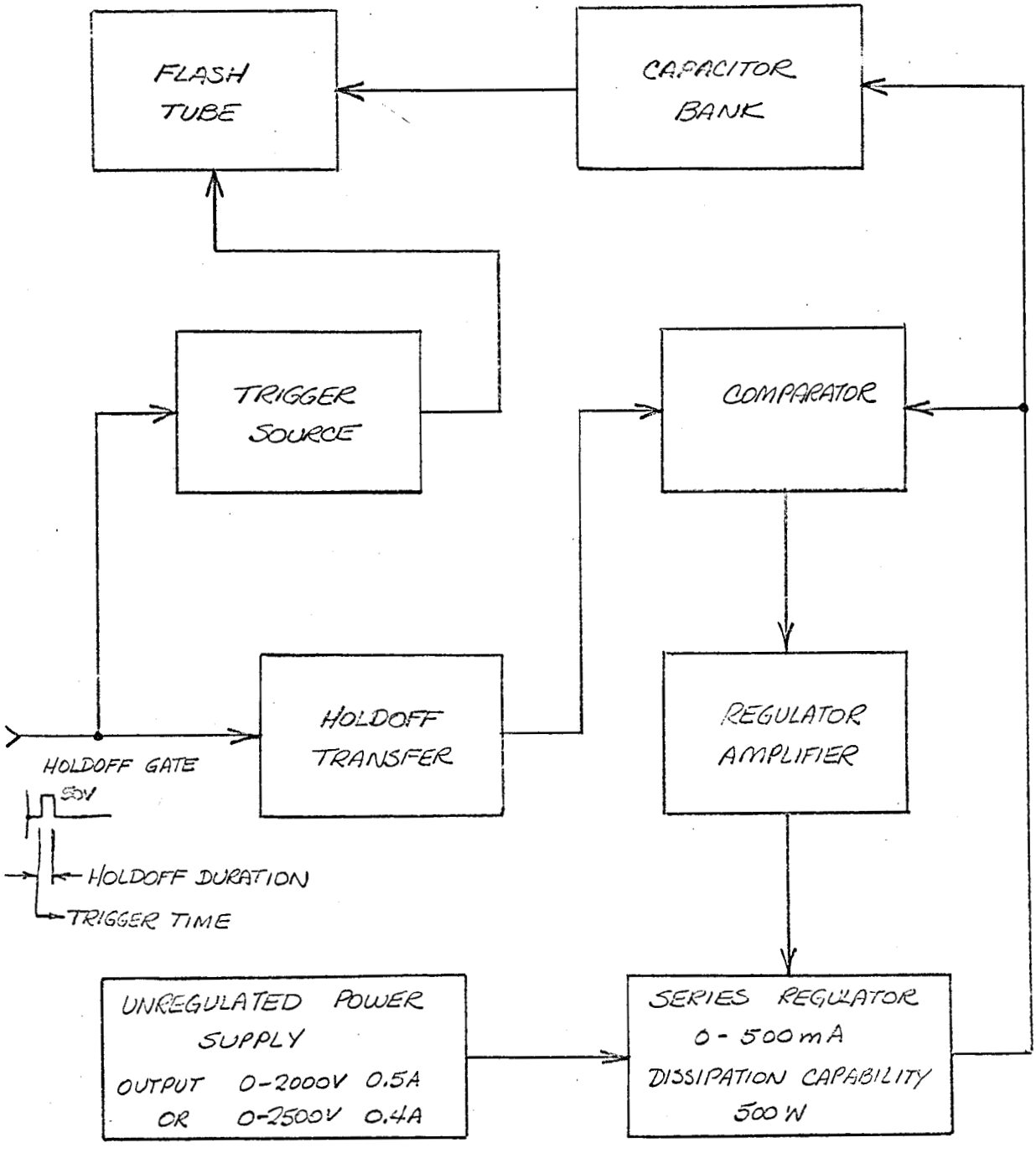

FLASH TUBE
CAPACITOR BANK
TRIGGER SOURCE
COMPARATOR
HOLDOFF TRANSFER
REGULATOR AMPLIFIER
HOLDOFF GATE
50V
HOLDOFF DURATION
TRIGGER TIME
UNREGULATED POWER SUPPLY
OUTPUT 0-2000V 0.5A
OR 0-2500V 0.4A
SERIES REGULATOR
0 - 500 mA
DISSIPATION CAPABILITY
500 W

FIG. 4

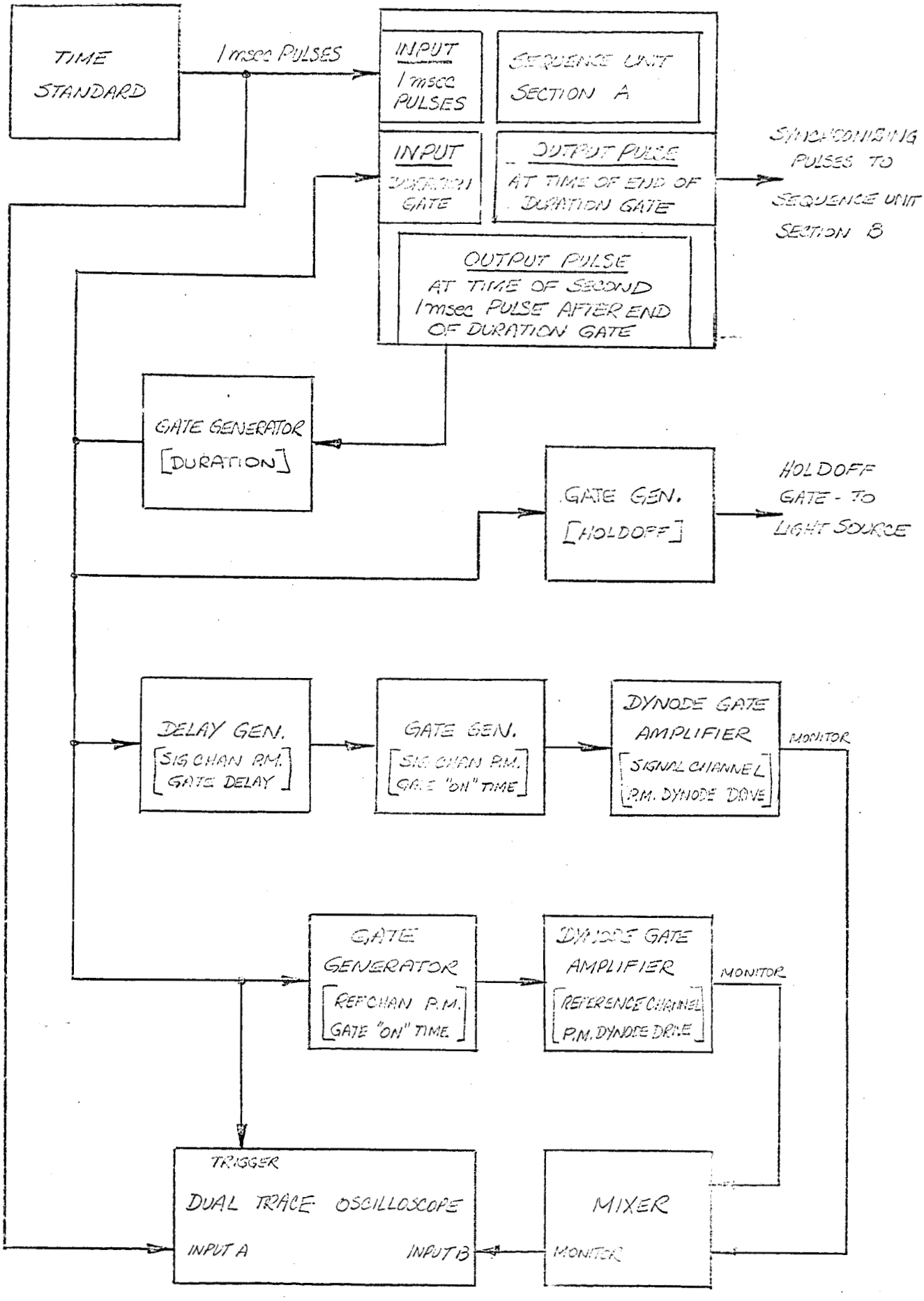

TIME STANDARD
1 msec PULSES
INPUT 1 msec PULSES
SEQUENCE UNIT SECTION A
INPUT DURATION GATE
OUTPUT PULSE AT TIME OF END OF DURATION GATE
SYNCHRONIZING PULSES TO SEQUENCE UNIT SECTION B
OUTPUT PULSE AT TIME OF SECOND 1 msec PULSE AFTER END OF DURATION GATE
GATE GENERATOR [DURATION]
GATE GEN. [HOLDOFF]
HOLDOFF GATE - TO LIGHT SOURCE
DELAY GEN. [SIG CHAN P.M. GATE DELAY]
GATE GEN. [SIG CHAN P.M. GATE "ON" TIME]
DYNODE GATE AMPLIFIER [SIGNAL CHANNEL P.M. DYNODE DRIVE]
MONITOR
GATE GENERATOR [REF CHAN P.M. GATE "ON" TIME]
DYNODE GATE AMPLIFIER [REFERENCE CHANNEL P.M. DYNODE DRIVE]
MONITOR
TRIGGER
DUAL TRACE OSCILLOSCOPE
INPUT A
INPUT B
MIXER
MONITOR

FIG. 5

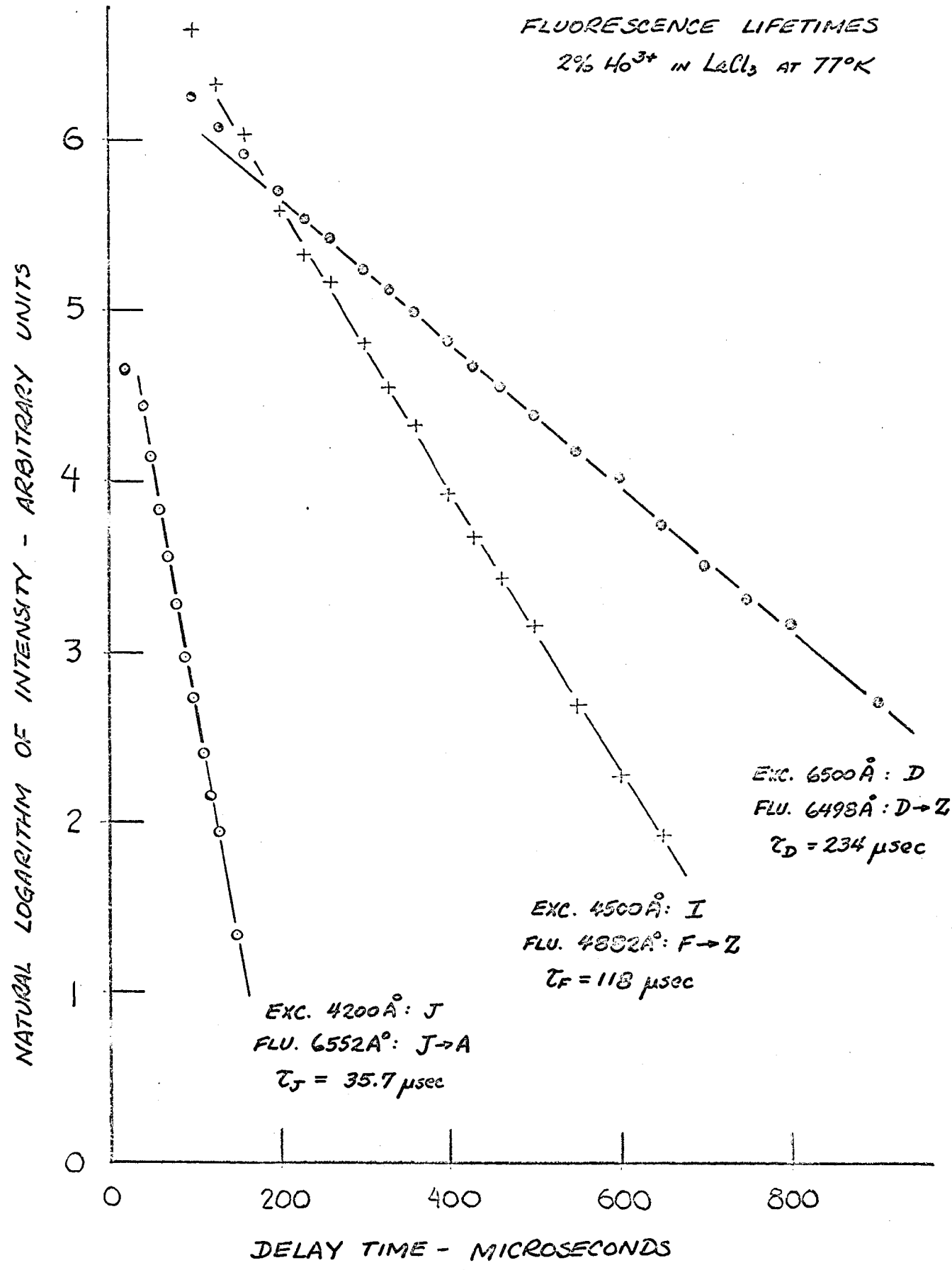

FLUORESCENCE LIFETIMES
2% Ho^{3+} IN $LaCl_3$ AT 77°K
NATURAL LOGARITHM OF INTENSITY - ARBITRARY UNITS
0
1
2
3
4
5
6
0
200
400
600
800
DELAY TIME - MICROSECONDS
EXC. 6500Å : D
FLU. 6498Å : D→Z
τ_D = 234 μsec
EXC. 4500Å: I
FLU. 4882A°: F→Z
τ_F = 118 μsec
EXC. 4200Å: J
FLU. 6552A°: J→A
τ_J = 35.7 μsec

FIG. 6